Pergamon

Tetrahedron Letters, Vol. 35, No. 7, pp. 1109-1112, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(93)E0424-I

SYNTHESIS OF BIDENTATE MIXED DONOR PHOSPHORUS/NITROGEN LIGANDS

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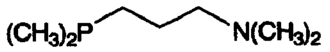
Abstract. 3-(*N,N*-Dimethylamino)-1-(dimethylphosphino)propane was synthesised by the photochemical addition of one equivalent of dimethylphosphine to *N,N*-dimethylallylamine. Synthesis of 2-(*N,N*-dimethylamino)dimethylphosphinoethane was achieved by the reaction of tetramethyldiphosphine with *N,N*-dimethyl-2-chloroethylamine.

Bidentate bis(phosphine) compounds $R_2P(CH_2)_nPR_2$ (R=alkyl, aryl) have developed into a versatile and important class of chelating ligands for transition metals. The nature of the donor atoms and their substituents critically influences the reactivity of metal complexes, and the ability to vary both the steric and donor properties of the ligands enables the control or modification of the reactivity and accessibility of the metal centre. Modifying polyphosphine ligands to incorporate nitrogen donors in place of one or more phosphorus atoms maintains the complex stability afforded by chelation, yet differentiates the donor ability at one or more of the coordination points.

The design of metal complexes incorporating mixed-donor phosphorus/oxygen chelating ligands has been reviewed.[1] However, relatively few polydentate phosphorus/nitrogen ligands are known.[2] We report here an alternative synthesis of $(CH_3)_2PCH_2CH_2CH_2N(CH_3)_2$ **(1)**, and the synthesis of the previously unreported bidentate ligand $(CH_3)_2PCH_2CH_2N(CH_3)_2$ **(2)**.



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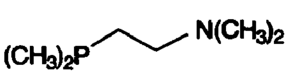

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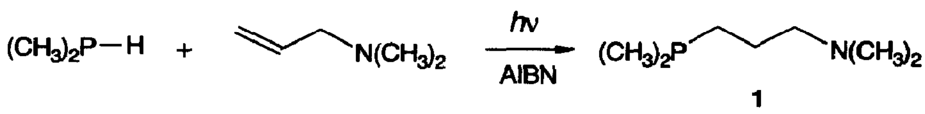
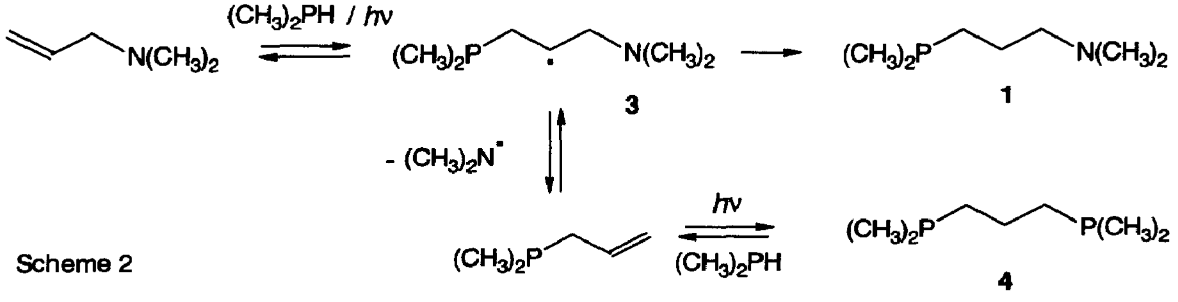
A synthesis of $(CH_3)_2PCH_2CH_2CH_2N(CH_3)_2$ (1) by the reaction of sodium dimethylphosphide with *N,N*-dimethyl-3-chloropropylamine has previously been reported.[3] By this approach, $(CH_3)_2PCH_2CH_2CH_2N(CH_3)_2$ can be made on a large scale but only in moderate yield. A more efficient photochemical approach employs the reaction of a primary phosphine with a suitable alkene[4] and the synthesis of (1) proceeds readily by the free radical addition of dimethylphosphine across the allylic double bond of *N,N*-dimethylallylamine (Scheme 1).



Scheme 1

In a typical reaction, a water-cooled pyrex well was charged with a solution of dimethylphosphine[5] (10.6 g, 0.17 mol), allyldimethylamine (9.46 ml, 0.08 mol) and AIBN (100 mg) in deoxygenated ether (150 ml) under an atmosphere of nitrogen. The entire apparatus was immersed in an ethanol bath, cooled to -20°C throughout the experiment. A 125W mercury immersion lamp was inserted into the cavity of the jacket, and the reaction mixture was irradiated. Nitrogen was bubbled through the mixture periodically to maintain mixing. The progress of the reaction was monitored by ^{31}P NMR, and the reaction was complete after 24 h of irradiation. Ether and remaining unreacted dimethylphosphine were distilled from the vessel leaving a crude product, which was further purified by distillation (Kugelrohr) to give $(CH_3)_2PCH_2CH_2CH_2N(CH_3)_2$ (**1**) (11.4 g, 97%) as a colourless oil b.p. 57°C/4.5 mm (lit[3] 36°C/3.0 mm). 3-(*N,N*-Dimethylamino)-1-(dimethylphosphino)propane (**1**) exhibits only a singlet in the $^{31}P\{^1H\}$ NMR spectrum[6] at δ -53.1 ppm.[7]

If the reaction is carried out without a large excess of the starting phosphine, the reaction rates are slowed, and the reaction fails to reach completion. The photochemical reaction probably proceeds via a free radical mechanism, involving the addition of a dimethylphosphinyl radical to the olefin to give (**3**), followed by hydrogen atom abstraction to give the product. The symmetrical bisphosphine $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$ (**4**) was isolated as a minor by-product from the reaction mixture. The formation of (**4**) is not unreasonable under the reaction conditions, since the loss of a dimethylaminyl radical from (**3**) could give rise to allyldimethylphosphine as an additional olefin substrate in the reaction mixture. The addition of dimethylphosphine to allyldimethylphosphine gives (**4**) as a reaction product (Scheme 2). The formation of (**4**) as a reaction by-product in a related reaction has been previously noted.[8]

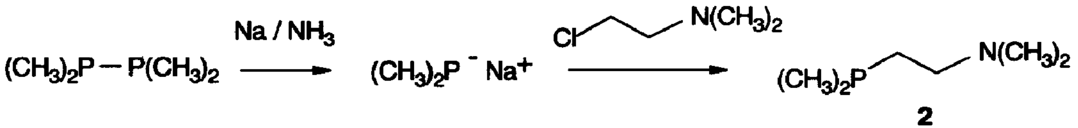


Scheme 2

An air stable phosphine sulfide derivative of $(CH_3)_2PCH_2CH_2CH_2N(CH_3)_2$ was prepared by stirring the compound (0.2 g, 1.36 mmol) with elemental sulfur powder (0.05 g, 1.6 mmol) in THF, under nitrogen for 24 h.

The resulting white precipitate of $(CH_3)_2P(S)CH_2CH_2CH_2N(CH_3)_2$ (**5**) (0.16 g, 67%) m.p. >220°C (dec.) was characterised spectroscopically.[9]

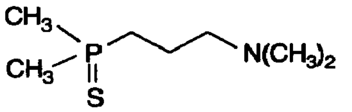
2-(*N,N*-dimethylamino)dimethylphosphinoethane (**2**) is a previously unreported compound and it was synthesised following an analogous procedure to that employed previously by Kordosky *et al*[3] for the synthesis of $(CH_3)_2PCH_2CH_2CH_2N(CH_3)_2$ (Scheme 3).



Scheme 3

In a typical reaction, freshly cut pieces of sodium (3.10 g, 0.13 mol) were added to liquid ammonia (200 ml) at -78°C, producing a dark blue solution. Tetramethyldiphosphine[3] (8.17 g, 0.07 mol) was added dropwise via a double ended needle, producing a dark olive-green colour.[10] *N,N*-Dimethyl-2-chloroethylamine (14.4 g, 0.13 mol) was added dropwise over the space of two hours, and the colour of the reaction mixture changed from green to brown, red, orange, yellow, and finally the mixture became a white turbid suspension. The ammonia was allowed to evaporate under a flow of nitrogen and the resulting white gum was extracted repeatedly with anhydrous, degassed ether. The solvent was removed from the combined ether layers by distillation at atmospheric pressure and the remaining crude product was distilled under vacuum (Kugelrohr) to give 2-(*N,N*-dimethylamino)dimethylphosphinoethane (**2**) (5.45 g, 31%) b.p. 45°C/4.0 mm Hg as a colourless, air-sensitive oil. The $^{31}P\{^1H\}$ NMR spectrum of (**2**) appears as a singlet at δ -54.3 ppm.[11]

An air stable phosphine sulfide derivative of $(CH_3)_2PCH_2CH_2N(CH_3)_2$ was prepared by stirring (**2**) with elemental sulfur powder in THF solution. The resulting white precipitate of $(CH_3)_2P(S)CH_2CH_2N(CH_3)_2$, (**6**), m.p. 125-129°C, was characterised spectroscopically.[12]



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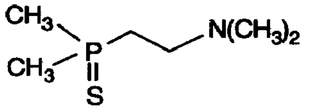

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Relative to DMPE [DMPE = 1,2-bis-(dimethylphosphino)ethane], (**2**) is a relatively weak coordinating ligand for iron and ruthenium. The ligand (**2**) only partially displaces the bulky and weakly coordinating DPrPE [DPrPE = 1,2-bis-(dipropylphosphino)ethane] from *trans*-$Fe(DPrPE)_2Cl_2$ to give a mixture of labile products. No displacement of DMPE is evident when (**2**) is mixed with *trans*-$Fe(DMPE)_2Cl_2$. No displacement of DPrPE from *trans*-$Fe(DPrPE)_2Cl_2$ is observed when the complex is mixed with (**1**). This indicates that (**1**) is a weaker ligand than (**2**) in terms of coordination to iron and this is not unexpected since the formation of 6-membered chelating ring is generally less favourable than formation of a 5-membered chelating ring in analogous systems.

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6. ^{31}P NMR spectra were recorded at 162.0 MHz and were referenced to external neat $(MeO)_3P$ taken to be 140.85 ppm.

7. $^1H\{^{31}P\}$ NMR spectrum of $(CH_3)_2PCH_2CH_2CH_2N(CH_3)_2$ (**1**) (benzene-d_6) : δ 2.423 (t, 2H, CH_2N); 2.310, (s, 6H, 2 x NCH_3); 1.750, (m, 2H, $CH_2CH_2CH_2$); 1.485, (t, 2H, CH_2P); 1.073, (s, 6H, 2 x PCH_3). $^{13}C\{^1H,^{31}P\}$ NMR spectrum (benzene-d_6) : δ 61.7, (CH_2N); 46.2, (2 x CH_3N); 30.8, ($CH_2CH_2CH_2$); 25.1, (CH_2P); 15.0, (2 x CH_3P).

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9. Selected spectral data for $(CH_3)_2P(S)CH_2CH_2CH_2N(CH_3)_2$ (**5**) : $^1H\{^{31}P\}$ NMR ($CDCl_3$) : δ 2.495 (t, $2H_a$, CH_2N, $^3J_{HaHm}$ = 7.0 Hz); 2.311, (s, 6H, 2 x NCH_3); 2.060, (t, 2H, CH_2P); 1.916, (m, $2H_m$, $CH_2CH_2CH_2$); 1.737, (s, 6H, 2 x PCH_3). Mass Spectrum (EI) *m/z* 179(30 M^+), 108(15), 93(19), 85(28), 75(16), 72(15), 58(100), 42(13); High resolution mass spectrum : Calc'd for $C_7H_{18}NPS$, 179.0897; found 179.0832.

10. Tetramethyldiphosphine is a solid at -78°C and the reaction must be stirred for sufficient time to allow dissolution and formation of the phosphide reagent.

11. Selected spectral data for $(CH_3)_2PCH_2CH_2N(CH_3)_2$ (**2**) : $^1H\{^{31}P\}$ NMR (benzene-d_6) : δ 2.55, (t, $2H_a$, CH_2P); 2.31, (s, 6H, 2 x CH_3P); 1.63, (t, $2H_m$, CH_2P, $^3J_{HaHm}$ = 7.7 Hz); 1.09, (s, 6H, 2 x CH_3P). $^{13}C\{^1H,^{31}P\}$ NMR spectrum (d_6-benzene) : δ 57.6, (s, CH_2N); 45.9, (s, 2 x CH_3N); 31.6, (s, CH_2P); 15.1, (s, 2 x CH_3P).

12. Selected spectral data for $(CH_3)_2P(S)CH_2CH_2N(CH_3)_2$ (**6**) : $^1H\{^{31}P\}$ NMR ($CDCl_3$) : δ 2.679, (t, 2H, CH_2N); 2.359, (s, 6H, 2 x CH_3N); 2.062, (t, 2H, CH_2P); 1.765, (s, 6H, 2 x CH_3P). $^{13}C\{^1H,^{31}P\}$ NMR ($CDCl_3$) : δ 53.2, (CH_2N); 45.1, (2 x CH_3N); 32.6, (CH_2P); 21.3, (2 x CH_3P). Mass Spectrum (EI) *m/z* 165(11, M^+), 72(17), 71(100), 58(24), 56(14), 43(10), 42(12).

(*Received in UK* 15 *September* 1993; *revised* 15 *December* 1993; *accepted* 17 *December* 1993)